

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 384 540
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90200414.2

(51) Int. Cl.⁵: **C10G 67/06, C10G 53/08,
C07C 7/13**

(22) Date of filing: 21.02.90

(30) Priority: 24.02.89 US 315058

(43) Date of publication of application:
29.08.90 Bulletin 90/35

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI NL SE

(71) Applicant: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.**
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

(72) Inventor: **Stem, Stephen Charles**
4010-I, Highway 6 South, Apartment 162
Houston, Texas 77082(US)
Inventor: **Evans, Wayne Errol**
1019 Lively Court
Richmond, Texas 77469(US)

(74) Representative: **Aalbers, Onno et al**
P.O. Box 302
NL-2501 CH The Hague(NL)

(54) **Process for isomerization of a hydrocarbon stream.**

(57) This invention relates to a process for isomerization of a hydrocarbon feed stream, by passing said feed stream prior to isomerization over a first shape-selective separatory molecular sieve having a pore size of 4.5 x 4.5A or smaller, to adsorb normal paraffins and over a second shape-selective separatory molecular sieve having a pore size intermediate 5.5 x 5.5 to 4.5 x 4.5A and excluding 4.5 x 4.5A, to adsorb mono-methyl-branched paraffins.

EP 0 384 540 A1

PROCESS FOR ISOMERIZATION OF A HYDROCARBON STREAM

This invention relates to a process for isomerization of a hydrocarbon feed stream, comprising normal paraffins, mono-methyl-branched paraffins and dimethyl-branched paraffins, which process comprises the use of a feed pretreatment preceding isomerization.

Maintenance of high octane gasolines by methods other than lead addition is of continuing interest to
 5 refiners. Two major techniques are available to acquire high octane gasoline pools without lead addition. First, hydrocarbons can be reformed in the presence of a reforming catalyst, such as a platinum rhenium catalyst, to a high octane gasoline. Second, normal paraffins can be isomerized to branched paraffins which possess higher octane qualities. The present invention concerns the latter of these two processes.

From the standpoint of increasing octane, it is desirable that hydrocarbons in gasoline have maximum
 10 branching. For example, methylpentanes have lower octane ratings than do dimethylbutanes, thus in an isomerization process it is beneficial to maximize the content of dimethylbutanes (dimethyl-branched paraffins) at the expense of methylpentanes (mono-methyl-branched paraffins). It has now been found that a means to accomplish this goal is to employ a pre-isomerization separation step using different shape selective molecular sieves. The overall combined product stream of this isomerization process contains an
 15 increased amount of dimethylbutanes, the most highly branched and highest octane of the C₆ saturates. This results in a direct octane enhancement to the resultant gasoline blending pool. In refineries which restrict production of gasoline due to octane limitations, this octane enhancement can permit increased gasoline production.

The present invention relates to a process for isomerization of a first hydrocarbon feed stream
 20 comprising normal paraffins, mono-methyl-branched paraffins, and dimethyl-branched paraffins, which process comprises:

a) passing said first hydrocarbon feed stream to a first feed separation zone comprising a first shape-selective separatory molecular sieve having a pore size of 4.5 x 4.5A or smaller, said pore size being
 25 sufficient to permit entry of said normal paraffins but restrictive to prohibit entry of mono-methyl-branched paraffins and dimethyl-branched paraffins, to produce a second hydrocarbon feed stream comprising said mono-methyl-branched paraffins and dimethyl-branched paraffins and a first isomerization zone feed stream comprising normal paraffins;

b) passing said second hydrocarbon stream of step a) to a second feed separation zone comprising
 30 a second shape-selective separatory molecular sieve having a pore size intermediate 5.5 x 5.5 to 4.5 x 4.5A and excluding 4.5 x 4.5A, said pore size being sufficient to permit entry of normal paraffins and mono-methyl-branched paraffins but restrictive to prohibit entry of dimethyl-branched paraffins;

c) separating, in said second feed separation zone, at separation conditions, by means of said
 35 second shape-selective separatory sieve, said dimethyl-branched paraffins from said mono-methyl-branched paraffins, and producing a second feed separation zone effluent stream and a second isomerization zone feed stream;

d) recovering from said second feed separation zone a second feed separation zone effluent stream comprising said dimethyl-branched paraffins;

e) recovering from said first feed separation zone a first isomerization zone feed stream comprising
 40 said normal paraffins and recovering from said second feed separation zone a second isomerization zone feed stream comprising said mono-methyl-branched paraffins;

f) passing at least a portion of said first, said second or both said first and second isomerization zone
 feed streams to an isomerization zone maintained at isomerization conditions and containing an isomerization catalyst to produce an isomerization zone effluent stream comprising dimethyl-branched paraffins, mono-methyl-branched paraffins and normal paraffins.

45 Suitably, the hydrocarbon feed stream comprises paraffins containing 4 to 7 carbon atoms, preferably the feed stream comprises normal hexane, monomethyl pentanes and dimethyl butane.

The present invention is concerned with the novel use of a multiple select adsorbent molecular sieve system having particular separatory qualities. The sieves are arranged upstream of an isomerization
 50 process to treat a feed stream in order to preserve constituents in the feed stream which would be diminished in value by isomerization. Preferably, the multiple separatory sieve system of this invention comprises a first molecular sieve having a pore size of 4.5 x 4.5A and being shaped to permit adsorption of normal paraffins in a selective manner vis-a-vis monomethyl-branched paraffins, dimethyl-branched paraffins, cyclic paraffins and aromatic hydrocarbons and a second molecular sieve having a pore size of 5.5 x 5.5 to 4.5 x 4.5A excluding 4.5 x 4.5A, being selected to permit adsorption of mono-methyl-branched paraffins (and any ancillary normal paraffins) in deference to multi-branched paraffins, cyclic paraffins and

aromatic hydrocarbons which can be passed directly to a refinery gasoline blending pool.

Feed streams which are preferably used comprise saturated hydrocarbons having C_6 or greater carbon atoms. Preferably, the feed stream contains an amount of dimethyl-branched paraffinic hydrocarbons. The feed stream can comprise normal paraffins, mono-methyl-branched paraffins and dimethyl-branched paraffins. The feed streams are usually derived from refinery operations and can contain quantities of C_5^- , C_7^+ , and cyclic paraffins. Olefinic and aromatic hydrocarbons may also be present. When naphthenes and aromatics are present, they will suitably not be significantly adsorbed by the sieve upstream of isomerization and will pass with the dimethyl-branched paraffins directly to the refinery gasoline blending pool without isomerization. This is advantageous due to the relatively high octane quality of some of the aromatic and naphthenic material derived from this separation. Preferably the first hydrocarbon feed stream comprises normal hexane, mono-methyl-pentanes and dimethyl-butane.

Preferred feed streams contain more than 25 mole percent normal hexane.

The multiple molecular sieve pretreatment step which produces the hydrocarbon stream ultimately passed to the isomerization zone comprises at least two molecular sieves. These can be arranged in separate vessels, or they can be arranged in a stacked flow scheme within one vessel.

The first molecular sieve has a pore size of 4.5 x 4.5A or smaller to permit adsorption of normal paraffins and restrictive to prevent adsorption of mono-methyl-branched paraffins and dimethyl-branched paraffins. This first sieve can be a calcium 5A zeolite or any other sieve of similar pore dimensions. It is not necessary to size the first sieve to adsorb all of the normal paraffins, but it is preferred so that the second molecular sieve does not have to function as a normal paraffin adsorption sieve.

The second sieve in this process sequence is exemplified by a molecular sieve which has eight and ten member rings and pore dimensions intermediate 5.5 x 5.5 and 4.5 x 4.5A, excluding 4.5 x 4.5A.

The preferred second molecular sieve of this invention is exemplified by a ferrierite molecular sieve. It is preferred that the ferrierite sieve be present in a hydrogen form, but it alternatively can be exchanged with a cation of an alkali metal, or alkaline earth metal or transition metal cation. The molecular sieves of this invention include ferrierite and other analogous shape-selective materials with pore openings intermediate in dimensions to those of the calcium 5A zeolite and ZSM-5. Other examples of crystalline sieves include aluminophosphates, silicoaluminophosphates, and borosilicates.

The aluminophosphate, silicoaluminophosphate and borosilicate molecular sieves which can be used as a second molecular sieve will have a pore opening intermediate between 5.5 x 5.5 and 4.5 x 4.5A but excluding 4.5 x 4.5A.

It is feasible that the molecular sieve comprises a large pore zeolite that has been ion exchanged with cations to diminish the effective pore size of the sieve to within the aforementioned range of dimensions.

The sequence of the sieves, whether in discrete vessels or in a stacked variety, is very important to this invention. If the sieves are interchanged the process loses its effectiveness because the larger sieve will rapidly fill with normal paraffins, prohibiting the efficient adsorption of mono-methyl-branched paraffins.

The respective sieves should be arranged in a process sequence to first provide adequate adsorption of the normal paraffin hydrocarbons, and then, adsorption of the mono-methyl-branched paraffins. Each of the respective sieves can be provided with a common desorbent stream or each sieve may have its own desorbent stream. The desorbent is preferably a gaseous material such as a hydrogen gas stream, which will not have a deleterious effect upon subsequent downstream isomerization. Any of the hydrocarbons desorbed from these sieves by the desorbent, in addition to the hydrogen, can be passed together or separately to an isomerization zone. The desorbent stream from the first molecular sieve (hydrogen + n-paraffins) can be passed to an isomerization zone containing a catalyst selected for the isomerization of normal paraffin hydrocarbons while the desorbent and mono-methyl-branched paraffins derived from the second molecular sieve can be passed to an isomerization zone possessing a catalyst selected for the isomerization of these paraffins.

The adsorption/desorption conditions typically utilized with either or both of the molecular sieves of this invention comprise a temperature of from 75 °C to 400 °C and a pressure of from 2 bar to 50 bar. The adsorption and desorption conditions are very similar to the conditions present in the separation sieve or sieves normally operated downstream of isomerization.

The isomerization catalyst applied in the isomerization zone is preferably a zeolite with a catalytic metal dispersed thereon. Exemplary of such a catalyst is mordenite with platinum present in a range of 0.005 wt% to 10.0 wt% with a preferred range being from 0.2 to 0.4 wt%. Other zeolite molecular sieves are also viable which have a silica to alumina molar ratio of more than 3 and less than 60 and preferably less than 15. The zeolite molecular sieves can be exchanged with alkali metals or alkaline earth metals. The catalytic metals associated with the isomerization function are preferably noble metals from Group VIII of the Periodic Table of elements, such as platinum, palladium, osmium and/or ruthenium. The isomerization catalyst can

be present per se or it may be mixed with a binder material.

The isomerization conditions present in the isomerization zone are those selected to maximize the conversion of normal paraffins and mono-methyl-branched paraffins to dimethyl-branched paraffins. Preferably, the isomerization is carried out in the vapour phase with a fixed bed of isomerization catalyst. Typically the process is carried out at a temperature from 200 to 400 °C and a pressure of 10 to 40 bar. The isomerization process is limited in octane upgrading by thermodynamic equilibrium. Even at select conditions, the effluent from the isomerization reactor will still contain substantial amounts of normal paraffins and mono-methyl-branched paraffins which are unreacted or partially reacted due to the aforementioned equilibrium. Preferably, the first isomerization zone feed stream of step (e) is passed to a first isomerization zone containing an isomerization catalyst to selectively isomerize normal paraffins to mono-methyl-branched paraffins and dimethyl-branched paraffins and/or the second isomerization zone feed stream of step (e) is passed to a second isomerization zone containing an isomerization catalyst to selectively isomerize mono-methyl-branched paraffins to dimethyl-branched paraffins. A portion of the first isomerization zone effluent stream and/or the second isomerization zone effluent stream can be recycled to the first feed separation zone.

One of the advantageous aspects of this invention is the fact that dimethyl-branched paraffins, cyclic paraffins and aromatics are not passed to the isomerization zone. The exclusion of the dimethyl-branched paraffins from the isomerization zone is advantageous for maximizing the quantity of dimethyl-branched paraffins produced during isomerization while at the same time, reducing the number of normal paraffins which remain unisomerized in the isomerization zone effluent stream. After isomerization, the isomerization zone feed stream will contain unisomerized normal paraffins, mono-methyl-branched paraffins and dimethyl-branched paraffins.

The isomerization zone effluent stream, after suitable removal of light ends which are sometimes generated during isomerization, can be sent directly to the gasoline pool or it can be passed to a separation zone which will preferably comprise from three to eight adsorbent beds which can be modified to operate in an adsorption/desorption mode as exemplified in U.S. Patent 4,210,771. This first product separation zone can contain a calcium 5A zeolite sufficient to permit adsorption of the normal paraffins and restrictive to prevent adsorption of the mono-methyl-branched paraffins and dimethyl-branched paraffins.

A multiple, sequential molecular sieve such as used in the instant separatory sieve upstream of isomerization can be utilized to form a recycle stream of mono-methyl-branched paraffins and normal paraffins. The aforementioned examples of particular molecular sieves are exemplary of molecular sieves which can be utilized to separate the isomerization zone effluent stream. It is not necessary that all of the normal paraffins or all of the mono-methyl-branched paraffins and normal paraffins be recycled to the isomerization zone. Preferably, a portion of the isomerization zone effluent stream is passed to a first product separation zone containing a select shape-selective molecular sieve to separate at effluent stream separation conditions dimethyl-branched paraffins and optionally mono-methyl-branched paraffins from the isomerization zone effluent stream and to form an isomerization zone recycle stream comprising normal paraffins and optionally mono-methyl-branched paraffins; and recovering at least a portion of the dimethyl-branched paraffins and optionally mono-methyl-branched paraffins as a first product separation zone effluent stream. However, for economic purposes it is sometimes beneficial that all paraffins which are branched with a single methyl-moiety be recycled until an equilibrium is reached maximizing the quantity of dimethyl-branched paraffins.

In later process steps, two gasoline blending component streams are acquired. First, the material which will elute through the preliminary sieve upstream of isomerization will contain very high octane paraffins. Preferably, the first and second hydrocarbon feed streams contain aromatic and naphthenic hydrocarbons by the use of a first and second shape-selective separatory sieve which are restrictive to prohibit entry of the aromatic and naphthenic hydrocarbons wherein the aromatic and naphthenic hydrocarbons are recovered in the second feed separation zone effluent stream. The second gasoline blending component will be derived downstream of the separatory sieve over which the isomerization zone effluent stream is passed. These two gasoline blending streams can be combined and utilized as a single blending component or they can be used individually. To attain further separation, the first product separation zone effluent stream comprising dimethyl-branched paraffins and mono-methyl-branched paraffins can be passed to a second product separation zone containing a shape-selective molecular sieve to separate, at separation conditions, dimethyl-branched paraffins from mono-methyl-branched paraffins and to form an isomerization zone recycle stream comprising mono-methyl-branched paraffins and recovering at least a portion of the dimethyl-branched paraffins as a second product separation zone effluent stream. Alternatively, the isomerization zone effluent stream can be separated to yield an isomerization zone recycle stream comprising normal paraffins which are recycled to the isomerization zone.

The isomerization zone effluent stream comprising dimethyl-branched paraffins and mono-methyl-branched paraffins can be separated by a separation means to provide a product separation zone effluent stream comprising dimethyl-branched paraffins and an isomerization zone recycle stream comprising mono-methyl-branched paraffins.

5 Alternatively, at least a portion of the isomerization zone effluent stream is recycled to the first and second feed separation zones. This permits the isomerate to be segregated simultaneously and in commingled association with the feed. Hereby capital cost is minimized and the complexity of operation is reduced. A more detailed description of the process of the present invention is given in the Figures described hereinafter.

10 Figure 1 schematically shows a process known from prior art.

Figure 2 schematically shows a process of the present invention in which a multiple number of molecular sieves is applied upstream of isomerization.

Figure 3 schematically shows a process of the present invention in which multiple molecular sieves are applied upstream and downstream of isomerization.

15 Figure 4 schematically shows a process of the present invention in which multiple molecular sieves are applied upstream of isomerization and a unitary molecular sieve is applied downstream of isomerization.

Figure 5 schematically shows a process of the present invention in which a multiple number of molecular sieves is applied upstream of isomerization, and in which the material separated from the multiple molecular sieves is passed to selective isomerization zones.

20 Figure 6 schematically shows a process of the present invention in which multiple molecular sieves are applied upstream of isomerization, and in which material removed from the molecular sieves is passed to separate selective isomerization zones which produce an isomerate which is separated by multiple molecular sieves downstream of isomerization.

25 Figure 7 schematically shows a flow scheme of the process of the present invention in which, like Figure 6, separate isomerization zones are applied for each desorbate from the select, sequential molecular sieves upstream of isomerization.

In Figure 1 a feed stream comprising a fresh feed having, for example, 4 mol% C₁ to C₅; and 93 mol% C₆ paraffins with small quantities of cycloparaffins, aromatics, and C₇ + paraffins are passed through conduit 1 into a separatory zone 3 having at least three and preferably up to 8 adsorbent beds of a molecular sieve such as a calcium 5A zeolite sieve to separate feed constituents. The calcium 5A zeolite will entrap or adsorb normal paraffins while allowing mono-methyl-branched paraffins and other branched paraffins to pass through the separation zone and be used as a gasoline blending component. After applicable desorption with means not shown, a normal paraffin stream is withdrawn from the separatory zone 3 via conduit 7 and passed to isomerization zone 9. This zone is maintained at conditions selected to maximize the degree of branching of the product stream 11 and a typical isomerization catalyst will be present. If desirable, a vented hydrogen or light hydrocarbon gas stream can be removed from the isomerization zone via conduit 13. An effluent stream from isomerization zone 9 is removed via conduit 11, containing normal paraffins, mono-methyl-branched paraffins and more highly branched paraffins (e.g. ethylpentane, dimethylbutane etc.).

40 In Figure 2 a process of the present invention is shown, wherein a hydrocarbon feed stream is used similar to the one used in the process shown in Figure 1, in which a multiple number of select molecular sieves is used upstream of isomerization. The feed stream in conduit 101 is passed to separation zone 103 which may comprise either a stacked configuration or can comprise a series flow of vessels in a unitary configuration. Separation zone 103 contains at least two molecular sieves 105 and 107. These sieves may be separated by a holding chamber or separate conduit 109.

Molecular sieve #1 (105) is a zeolite having pore size of from 4.5 to 4.5A or smaller. A calcium 5A zeolite is preferably used. Molecular sieve 107, referred to as molecular sieve #2, has a pore size of 5.5 x 5.5 to 4.5 x 4.5A but excludes 4.5 x 4.5A. This molecular sieve will preferably comprise a ferrierite.

50 The first molecular sieve 105 selectively adsorbs normal paraffins in preference to mono-methyl-branched paraffins, multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons. After the normal paraffins have been substantially removed from the feed stream, contact is made with molecular sieve #2 (107). In this particular sieve, mono-methyl-branched paraffins are adsorbed while multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons are passed through the sieve without adsorption. The multi-branched paraffins, cyclic paraffins and aromatics have a high octane rating and are removed from separation zone 103 via conduit 111 and passed directly to refinery gasoline pool 113 for further blending with gasoline-based components. The normal paraffins can be desorbed from sieve 105 by means of a desorbent, preferably hydrogen, added to sieve 105 through conduit 115. If desired, a separate desorbent can be added to sieve 107 through conduit 117 or, in the alternative, if a unitary vessel is utilized in a

stacked-bed configuration, the desorbent may simply be added at one end of separation zone 103.

The material removed from sieve 107 via conduit 119 comprises the isomerization zone feed stream. This feed stream will contain a mixture of normal paraffins and mono-methyl-branched paraffins which are added to isomerization zone 121.

5 In isomerization zone 121, a molecular sieve isomerization catalyst is located to selectively convert normal paraffins to mono-methyl-branched paraffins and dimethyl-branched paraffins and to convert mono-methyl-paraffins to dimethyl-branched paraffins. The chemical equilibrium in the isomerization zone results in a mixture removed from isomerization zone 121 via conduit 123 comprising dimethyl-branched paraffins, normal paraffins and mono-methyl-branched paraffins. Without further separation, this stream can be
10 divided into a recycle stream 125 and passed back to the feed stream in conduit 101 or passed to product stream 127, which can be added directly to gasoline blending pool 113 or diverted through line 129 and added to conduit 111. The hydrocarbon content in conduit 127 (the isomerate) can alternatively be utilized separate and distinct from that high octane material added to refinery gasoline pool 113 via conduit 111. The recycle stream in conduit 125 can be added to feed stream 101 or to either separatory sieve 105 or
15 107. It is also possible to add recycle stream 125 directly to isomerization zone 121.

In Figure 3 the use of a process of the present invention is shown, wherein a hydrocarbon feed stream is used similar to the one used in the process shown in Figure 1. The feed stream is added via conduit 201 to separation zone 203. The separation zone may comprise either a series of separatory sieves individually located or, in the alternative, a stacked bed of sieves containing both of the applicable molecular sieves. For
20 sake of convenience, the drawings show the multiple number of sieves as molecular sieve #1 (205) and molecular sieve #2 (207). An intermediate zone 209 is present, but is not necessary to the functioning of this particular process.

Molecular sieve #1 (205) comprises a sieve having a pore dimension of 4.5 x 4.5A or smaller. Exemplary of this sieve is a calcium 5A zeolite. This sieve is selected for its ability to adsorb normal
25 paraffins.

Sieve 207 is exemplified as molecular sieve #2 and has a pore dimension of from about 5.5 x 5.5 to 4.5 x 4.5A, excluding 4.5A. A ferrierite type of molecular sieve exemplifies this type of sieve which is selective for the adsorption of normal paraffins, if any remain from sieve 205, and for mono methyl branched paraffins.

30 Dimethyl-branched paraffins or multi-branched paraffins, in addition to cyclic paraffins and aromatics, are removed via conduit 211 and passed to gasoline blending pool 213 for blending with a gasoline-based material. The normal paraffins adsorbed in sieve 205 and the mono-methyl-branched paraffins adsorbed in conduit 207 are desorbed through the use of a desorbent such as hydrogen added through conduits 215 and/or 217 to separation zone 203. Hydrocarbon material is withdrawn via conduit 219 and passed to
35 isomerization zone 221. The hydrocarbon material in conduit 219 comprises normal paraffins and mono-methyl-branched paraffins. Isomerization zone 221 contains an isomerization catalyst and is maintained at isomerization conditions to convert the normal paraffins to mono-methyl-branched paraffins and the mono-methyl-branched paraffins to dimethyl-branched paraffins. The effluent from isomerization zone 221 is withdrawn via conduit 223 and contains multi-branched paraffins in addition to normal paraffins and mono-methyl-branched paraffins. It is advantageous to separate the normal paraffins for recycle to ultimate
40 isomerization. For this reason, a first separation zone 224 is provided having a molecular sieve of pore dimensions of 4.5 x 4.5A or smaller. This separation produces a normal paraffin recycle stream withdrawn from separator 224 through conduit 225, which is recycled to the isomerization zone 221 through conduit 227. The effluent (non-adsorbed hydrocarbons) from separation zone 224 is withdrawn via conduit 229 and
45 usually comprises dimethyl-branched paraffins and mono-methyl-branched paraffins. It is advantageous to recycle mono-methyl-branched paraffins to isomerization zone 221. For this reason, stream 229 is added to separation zone 231 for separation of the dimethyl-branched paraffins from the mono-methyl-branched paraffins. Separation zone 231 contains a molecular sieve having a pore dimension of 5.5 x 5.5 to 4.5 x 4.5A excluding 4.5 x 4.5A. A recycle stream is removed from separator 231 via conduit 233. The contents
50 of this stream will predominantly consist of mono-methyl-branched paraffins which are added to the recycle stream of conduit 225 to form recycle stream 227.

A stream comprising multi-branched paraffins (isomerate) is withdrawn from second separation zone 231 via conduit 235 and passed to a second blending pool 237 for use in blending with a gasoline range boiling material. It is within the scope of this invention that blending pool 213 and blending pool 237
65 comprise the same zone or they may be operated independent of one another.

In Figure 4 the use of a process of the present invention is shown, wherein a hydrocarbon feed stream is used similar to the one used in the process shown in Figure 2. A feed stream in conduit 301 is added to separation zone 303 which comprises at least two different molecular sieves. These sieves may be in a

stacked bed configuration or in a series flow configuration in one or more vessels. Molecular sieve #1 (305) comprises a molecular sieve having a pore dimension of between 4.5 x 4.5A or smaller. Calcium 5A zeolite is an example of one such sieve. Molecular sieve #2 (307) has a pore diameter of between 5.5 x 5.5 to 4.5 x 4.5A excluding 4.5 x 4.5A and is exemplified by ferrierite. An intermediate void space is shown as 309, which is optional and not necessary to have an operable process. It is also contemplated that these sieves comprise a multiple number of alternating sieves, such that when one sieve is being desorbed another is being used as an adsorbent. A desorbent material is added to sieve 305 through conduit 350 and sieve 307 through conduit 311 in order to desorb the respective normal paraffins and mono methyl paraffins and form a feed separation zone effluent stream 313. A blending stream comprising cyclic paraffins, aromatic paraffins and multi-branched paraffins is removed from zone 307 via conduit 315 and passed to blending pool 317 for use in the manufacture of gasoline. Effluent stream 313 comprises a feed material for isomerization zone 319. This zone contains an isomerization catalyst and is maintained at isomerization conditions to produce a maximum quantity of dimethyl-branched paraffins from the normal paraffins and mono-methyl-branched paraffins. The effluent from isomerization zone 319 is removed via conduit 321 and contains normal paraffins, mono-methyl-branched paraffins and dimethyl-branched paraffins. These materials are added to separation zone 323, which can contain either a calcium 5A zeolite, a ferrierite-type sieve or a combination of both. Depending on the type of sieve present in separation zone 323, a blending component (isomerate) is removed via conduit 325 and passed to blending pool 317. If desired, this blending material can be removed from separation zone 323 via conduit 327 and added to a second blending pool 329. Where the separatory sieve is a calcium 5A zeolite, isomerization zone recycle stream 331 will comprise normal paraffins, while streams 325 and 327 will comprise mono-methyl-branched paraffins. In an embodiment where separation zone 323 is a ferrierite-type molecular sieve, isomerization zone recycle stream 331 will comprise normal paraffins and mono-methyl-branched paraffins while blending streams 325 and 327 will mainly comprise dimethyl-branched paraffins.

In Figure 5 the use of a process of the present invention is shown, wherein a hydrocarbon feed stream is used similar to the one used in the process shown in Figure 1 with the advantage that the select separation of the feed stream will provide feed to different selective isomerization reactors. Feed stream 401 contains normal paraffins, mono-methyl-branched paraffins, multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons which are passed to molecular sieve #1 (shown as 403). This molecular sieve will preferably be in a discrete vessel in order to selectively adsorb normal paraffins from the feed material. A desorbent such as hydrogen may be added through conduit 405 to remove the adsorbed normal paraffins after the flow of the feed material in conduit 401 is stopped. Unadsorbed effluent from sieve #1 (403) comprising mono-methyl-branched paraffins, multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons is removed via conduit 407 and passed to molecular sieve #2 (409) having a pore size of 5.5 x 5.5 to 4.5 x 4.5A and excluding 4.5 x 4.5A, e.g. ferrierite. A desorbent such as hydrogen may be added via conduit 411 to remove the mono-methyl-branched paraffins adsorbed by sieve 409.

A high octane product of this invention is removed in conduit 413 which contains multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons. This material is added to gasoline blending pool 415. Each sieve, 403 and 409, is responsible for providing an effluent respectively shown as 417 and 419. Effluent stream 417 contains desorbent and normal paraffins. These are added to first isomerization zone 424 which contains an isomerization catalyst selective for the conversion of the normal paraffins to mono-methyl-branched paraffins and multi-branched paraffins. The conditions maintained in isomerization zone 424 are those conditions which are most conducive to the preparation of the multi-branched paraffins. An isomerate is removed via conduit 423 from isomerization zone 424 and is passed to isomerate separation zone 425 for separation of the high-octane valued materials from the low-octane valued materials. The multi-branched or, if desired, mono-methyl-branched paraffins can be removed as gasoline blending agents via conduit 427 and used as appropriate or the same may be blended into gasoline pool 415. Depending on the separation qualities of the sieve in the isomerate separation zones a separation effluent is provided in withdrawal conduit 429.

The effluent from molecular sieve 409 in conduit 419 comprises mainly mono-methyl-branched paraffins which are passed to isomerization zone 429 maintained at conditions selected to cause maximum conversion of mono-methyl-branched paraffins to multi-branched paraffins. An isomerization catalyst is present in isomerization zone 429 which is chosen to maximize the production of multi-branched paraffins from mono-methyl-branched paraffins. The effluent from isomerization zone 429 is removed as a second isomerate stream 431 and passed to isomerate separation zone 425. Isomerate stream 431 will comprise mono-methyl-branched paraffins and dimethyl-branched paraffins. Separation will be effected on the components of stream 431 as well as those of similar components in stream 423 and withdrawn in withdrawal conduit 429. This may be divided into recycle stream 433 (passed to isomerization zone 429) or

conduit 435 (passed to isomerization zone 424). Either of these two recycle streams may be mixed or added at other places in the process.

In Figure 6 the use of a process of the present invention is shown, wherein a hydrocarbon feed stream is used similar to the one used in the process in Figure 1 with the advantageous use of multiple isomerization reactors connected to multiple separatory sieves. A feed stream 501 comprising normal paraffins, mono-methyl-branched paraffins, multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons is passed to molecular sieve unit 503 which contains molecular sieve #1 (505). This molecular sieve has a pore dimension of 4.5 to 4.5A or smaller and can be exemplified by a calcium 5A zeolite. This sieve adsorbs normal paraffins. The unadsorbed effluent from the first molecular sieve 505 is withdrawn from zone 503 via conduit 509 and contains mono-methyl-branched paraffins, multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons. This material is utilized as a feed for the second molecular sieve contained in separatory unit 511, shown as sieve 513. This sieve has a pore dimension of about 5.5 x 5.5 to 4.5 x 4.5A excluding 4.5 x 4.5A. This high octane stream may be removed as a blending material via conduit 515 and passed to blending pool 517. Where desired, a desorbent stream 519 may be provided to remove mono-methyl-branched paraffins from sieve 513 which leaves separation unit 511 via conduit 521. Desorbent added via conduit 507 to sieve 505 will result in the removal of desorbent and normal paraffin from unit 503 via conduit 523. This material is added to isomerization zone 525 wherein an isomerization catalyst is maintained at isomerization conditions effective to result in the maximum production of multi-branched paraffins from the normal paraffins of the feed material in conduit 523. The isomerization zone effluent is removed via conduit 527 and will comprise normal paraffins, mono-methyl-branched paraffins and multi-branched paraffins. The hydrocarbon components in stream 527 are passed to a first separation zone 529 (referred to as separation zone #1A). This zone preferably comprises a molecular sieve 531 which is very similar in nature to molecular sieve 505. Normal paraffins are removed after desorption via conduit 533 and passed back to isomerization unit 525 by means of recycle conduit 535. Mono-methyl-branched paraffins and multi-branched paraffins pass unadsorbed through separation zone 529 via conduit 537 and pass to a second separation zone 539, (shown as separation zone #1B). A molecular sieve 541 is present in second separation zone 539 which is very similar to molecular sieve 513. An unadsorbed gasoline blending material (isomerate) comprising multi-branched paraffins is removed via conduit 543 and passed to gasoline blending pool 517 or utilized individually. A recycle stream is withdrawn from separation zone 539 via conduit 545 and is passed to isomerization zone 525, or alternatively a recycle stream is withdrawn via conduit 547 which is combined with desorbed normal paraffins passed through conduit 533, to form isomerization zone recycle stream 535.

The desorbed effluent from molecular sieve 513 in conduit 521 comprises predominantly mono-methyl-branched paraffins. These are added to isomerization zone 547 which contains an isomerization catalyst selected for its high conversion of mono-methyl-branched paraffins and maintained at isomerization conditions suitable to maximize the production of multi-branched paraffins from the mono-methyl-branched paraffins. An effluent stream is withdrawn from isomerization zone 547 via conduit 549 which comprises normal paraffins, mono-methyl-branched paraffins and dimethyl-branched paraffins. This stream is added to separation zone 551, (shown as separation zone #2A). The molecular sieve contained in separation zone 553 is very similar to sieve 505. A normal paraffin recycle stream can be desorbed therefrom and removed via conduit 555 and passed via conduit 567 to isomerization zone 547. The hydrocarbon stream minus the normal paraffins is removed from separation zone 553 via conduit 559 and passed to second separation zone 561, (shown as separation zone #2B). The molecular sieve contained therein, 563, is very similar to the molecular sieve 513. A mono-methyl-branched paraffins recycle stream is passed directly to isomerization reactor 547 via conduit 565. If necessary, a separate desorbent stream can be removed via conduit 567 and combined with the normal paraffins from conduit 555 to form recycle stream 567. A third blending component is obtained from separation sieve 563 containing mainly multi-branched paraffins in conduit 569 which are added to gasoline pool 517 or utilized as the refiner deems necessary in the blending of gasoline with the base materials.

Another process option is to pass stream 545 of Figure 6 comprising mono-methyl-branched hydrocarbons, to isomerization zone #2 (547) which contains a catalyst selected for its high conversion of mono-methyl-branched hydrocarbons to multiple branched hydrocarbons and operated at conditions to optimize isomerization of mono-methyl-branched hydrocarbons. A further process option is to pass stream 555 of Figure 6 which comprises normal paraffins to isomerization zone #1 (525) which contains a catalyst selected for its high conversion of normal paraffins and operated at conditions to optimize isomerization of normal paraffins.

The process shown in Figure 6 can be greatly simplified and reduced in capital cost as shown in Figure 7, in which process the effluents of both isomerization zones are recycled to the unsegregated feed. In this

way the molecular sieves on the feed perform both the feed segregation and the product segregation with great savings in capital costs and operational flexibility while enjoying the advantage of isomerization zones which are specifically optimized for the particular select desorbate. In Figure 7 a process is shown in which the sequentially arranged molecular sieves 605 and 613 segregate the feed components as well as the isomerates.

A feed stream is treated in respective molecular sieves 605 and 613 as shown in sieves 505 and 513 of Figure 6. Effluent from sieve 605 is passed to the first isomerization zone via conduit 623. This stream consists mainly of n-paraffins which are isomerized to mono-methyl-branched paraffins and dimethyl-branched paraffins. Effluent in stream 609 contains the hydrocarbon content of feed 601 minus the n-paraffins adsorbed in sieve 605. Passage to the second molecular sieve 613, having a pore size of 5.5 x 5.5 to 4.5 x 4.5A excluding 4.5 x 4.5A, results in adsorption of any n-paraffins remaining unadsorbed in sieve 605 and mono-methyl-branched paraffins. Dimethyl-branched paraffins, aromatics and cycloparaffins which are not adsorbed in either sieve 605 or 613 are passed to blending pool 617 via conduit 615.

Different isomerization catalysts are present in isomerization zones 625 and 647. The catalyst in zone 625 can be selected to maximize the isomerization of n-paraffins in conduit 623. The catalyst in zone 647 can be selected to maximize isomerization of the monomethyl pentanes in stream 621. Both of these respective zones produce effluents, respectively zone 625 effluent 627 and zone 647 effluent 649. These effluent streams can be passed in whole or in part back to pre-isomerization separation via conduit 661.

The invention is further illustrated by the following Examples.

EXAMPLE 1

In this example, sorption capacities of sodium ferrierite, calcium 5A zeolite and sodium ZSM-5 were determined in regard to normal hexane, 3-methylpentane and 2,3-dimethylbutane. The particular zeolite was placed on a pan in a Cahn balance, the sample chamber was evacuated, and heated to 550 °C for one hour. The particular zeolite was thus dried and following drying was cooled to 105 °C. Hydrocarbon vapours were admitted to the evacuated chamber to a level of 0.13 bar. Weight changes due to the adsorption of hydrocarbon into the zeolite were recorded. An exposure time of three hours was allowed for the branched hydrocarbons to approach equilibrium weight, whereas an exposure time of only one half hour was required for normal hexane. The results of this adsorption are shown in Table 1. Each combination of zeolite plus solvent was subjected to at least three separate determinations. Listed in the Table are results of individual determinations, as well as mean and standard deviation values for each set of determinations.

Table 1

Hydrocarbon	Weight of HC Adsorbed (mg/g)		
	Ca-5A	Na-Ferrierite	Na-ZSM-5
2,3-Dimethylbutane	1.6	2.1	59.4
	1.3	1.7	59.7
	1.9	1.9	61.1
	2.4	1.8	--
MEAN + STD DEV:	1.8 ± 0.4	1.9 ± 0.1	60.0 ± 0.9
3-Methylpentane	1.7	19.4	56.5
	1.9	19.6	63.9
	2.0	18.4	62.3
	1.5	--	--
MEAN + STD DEV:	1.7 ± 0.3	19.2 ± 0.5	60.9 ± 3.8
n-Hexane	92.3	55.4	111.9
	90.1	54.5	105.4
	100.7	53.9	106.7
	99.3	56.7	--
MEAN + STD DEV:	95.6 ± 4.5	55.2 ± 1.0	107.9 ± 3.4

The sorption capacities are reported as weight gain in the sieve relative to the dry weight of the pure zeolite. As shown in Table 1, the calcium 5A zeolite adsorbed very little branched hydrocarbon. The ratio of 3-methylpentane/normal hexane sorption capacities is 0.018. In contrast, sodium ferrierite adsorbed little dimethylbutane but adsorbed a substantial amount of 3-methylpentane. The ratio of the 3-methylpentane/normal hexane sorption capacity is about 20 times greater for the sodium ferrierite than for calcium 5A zeolite. The sodium ZSM-5 sieve adsorbed virtually identical amounts of the mono- and di-branched isomers. Thus, the aforescribed sodium ferrierite has the capability to effect a separation between 3-methylpentane and 2,3-dimethylbutane upstream of isomerization by capturing 3-methylpentane while permitting 2,3-dimethylbutane to elute and, thereby, has the capability to preserve the octane quality of the higher octane paraffin. Moreover, the sodium ferrierite treatment of a feed stream containing the aforementioned components will permit adsorption of both 3-methylpentane and normal hexane which can then be desorbed and passed to an isomerization zone for conversion to 2,3-dimethylbutane.

EXAMPLE 2

The sorption capacities of hydrogen ferrierite towards the same three hydrocarbons were determined and are presented in Table 2. The ratio of 3-methylpentane/normal hexane sorption for the hydrogen ferrierite is about 25 times greater than that for the calcium-5A sieve.

Table 2

Hydrocarbon	Na-Ferrierite	Ca-5A
2,3-Dimethylbutane	3.6	1.6
	3.3	1.3
	3.2	1.9
	3.1	2.4
MEAN + STD DEV:	3.3 ± 0.2	1.8 ± 0.4
3-Methylpentane	28.8	1.7
	28.6	1.9
	27.1	2.0
		1.5
	27.4	1.2
MEAN + STD DEV:	28.0 ± 0.8	1.7 ± 0.3
n-Hexane	56.5	92.3
		90.1
		100.7
		99.3
MEAN + STD DEV:	56.5	95.6 ± 4.5

EXAMPLE 3

A sample of ammonium ferrierite was tableted to 14-45 mesh and placed in a glass tube. The glass tube was placed in a tube furnace under a flow of nitrogen and heated to 500°C for 2 hours to expel ammonia and thus produce the hydrogen form of ferrierite. Under the same nitrogen flow, the molecular sieve was cooled to room temperature while the nitrogen flow was diverted through a gas saturation tower containing a mixture of normal hexane, 3-methylpentane and 2,3-dimethylbutane. The molecular sieves were exposed to hydrocarbon-containing streams of nitrogen for 1 hour. Samples of the hydrocarbon reservoir were taken at the beginning and at the end of the gas saturation period. The purpose of sampling both at the start and at the end of the experiment was to verify that the ratio of hydrocarbons remained essentially constant throughout the experiment. A portion of the hydrocarbon-containing vapour stream was diverted directly through a cold finger that was immersed in a dry ice/acetone bath to collect a sample of

the actual hydrocarbon vapours.

Following exposure to these vapours, the hydrocarbon-saturated ferrierite sample was removed from the glass tube and placed on a vacuum line. The sample was evacuated to below 0.001 bar through a cold finger immersed in liquid nitrogen. The sample was heated to 40°C and the sorbed hydrocarbon was removed from the zeolite. The results of the adsorption were analyzed by gas chromatography and are shown in Table 3.

Table 3

Competitive Sorption of Hexane Isomers By H-Ferrierite			
	%w	%w	%w
Sample	2,3-DMB	3-MP	n-hexane
Gas saturation tower contents at start of experiment	34.7	37.1	28.2
Gas saturation tower contents at end of experiment	26.7	36.8	36.5
Gaseous hydrocarbon stream	41.7	36.3	22.0
Hydrocarbon adsorbed by H-ferrierite	1.4	17.2	81.4

As shown in Table 3, very little dimethylbutane will enter the pores of hydrogen ferrierite. This is advantageous because thereby dimethylbutane is preserved upstream of isomerization. A substantial amount of mono-methylpentane will be captured by the sieve and can then be recovered and passed to the isomerization zone for its conversion to 2,3-dimethyl-butane. Moreover, the unconverted or partially converted mono-methyl-branched paraffins in the recycle stream (exemplified by conduit 125 in Figure 2) can be readily isomerized to exhaustion in comparison to a process operated without the molecular sieve of the instant invention upstream of the isomerization zone.

Claims

1. A process for isomerization of a first hydrocarbon feed stream comprising normal paraffins, mono-methyl-branched paraffins, and dimethyl-branched paraffins, which process comprises:

a) passing said first hydrocarbon feed stream to a first feed separation zone comprising a first shape-selective separatory molecular sieve having a pore size of 4.5 x 4.5Å or smaller, said pore size being sufficient to permit entry of said normal paraffins but restrictive to prohibit entry of mono-methyl-branched paraffins and dimethyl-branched paraffins, to produce a second hydrocarbon feed stream comprising said mono-methyl-branched paraffins and dimethyl-branched paraffins and a first isomerization zone feed stream comprising normal paraffins;

b) passing said second hydrocarbon feed stream of step a) to a second feed separation zone comprising a second shape-selective separatory molecular sieve having a pore size intermediate 5.5 x 5.5 to 4.5 x 4.5Å and excluding 4.5 x 4.5Å, said pore size being sufficient to permit entry of normal paraffins and mono-methyl-branched paraffins but restrictive to prohibit entry of dimethyl-branched paraffins;

c) separating, in said second feed separation zone, at separation conditions, by means of said second shape-selective separatory sieve, said dimethyl-branched paraffins from said mono-methyl-branched paraffins and producing a second feed separation zone effluent stream and a second isomerization zone feed stream;

d) recovering from said second feed separation zone a second feed separation zone effluent stream comprising said dimethyl-branched paraffins;

e) recovering from said first feed separation zone a first isomerization zone feed stream comprising said normal paraffins and recovering from said second feed separation zone a second isomerization zone feed stream comprising said mono-methyl-branched paraffins;

f) passing at least a portion of said first, said second or both said first and second isomerization zone feed streams to an isomerization zone, maintained at isomerization conditions, and containing an isomerization catalyst to produce an isomerization zone effluent stream comprising dimethyl-branched paraffins, mono-methyl-branched paraffins and normal paraffins.

2. The process of claim 1 wherein at least a portion of said isomerization zone effluent stream is passed to a first product separation zone containing a select shape-selective molecular sieve to separate, at effluent

stream separation conditions, said dimethyl-branched paraffins and optionally said mono-methyl-branched paraffins from said isomerization zone effluent stream and to form an isomerization zone recycle stream comprising normal paraffins and optionally mono-methyl-branched paraffins; and recovering at least a portion of said dimethyl-branched paraffins and optionally mono-methyl-branched paraffins as a first product separation zone effluent stream.

3. The process of claim 1 or 2 wherein said second shape-selective separatory molecular sieve comprises a ferrierite molecular sieve.

4. The process of any one of claims 1-3, wherein separation conditions maintained in said first feed separation zone and said second feed separation zone include a temperature of from 75 °C to 400 °C and a pressure of from 2 bar to 50 bar.

5. The process of any one of claims 1-4 wherein said first and said second hydrocarbon feed stream contain aromatic and naphthenic hydrocarbons and wherein said first and said second shape-selective separatory sieve are restrictive to prohibit entry of said aromatic and naphthenic hydrocarbons and wherein said aromatic and naphthenic hydrocarbons are recovered in said second feed separation zone effluent stream.

6. The process of any one of claims 2-5 wherein said first product separation zone contains a calcium 5A zeolite sufficient to permit adsorption of said normal paraffins and restrictive to prevent adsorption of said mono-methyl-branched paraffins and dimethyl-branched paraffins.

7. The process of any one of claims 2-6 wherein the first product separation zone effluent stream comprising dimethyl-branched paraffins and mono-methyl-branched paraffins is passed to a second product separation zone containing a shape-selective molecular sieve to separate, at separation conditions, dimethyl-branched paraffins from mono-methyl-branched paraffins and to form an isomerization zone recycle stream comprising mono-methyl-branched paraffins and recovering at least a portion of said dimethyl-branched paraffins as a second product separation zone effluent stream.

8. The process of any one of claims 1-7 wherein said isomerization zone effluent stream comprising dimethyl-branched paraffins and mono-methyl-branched paraffins is separated by a separation means to provide a product separation zone effluent stream comprising dimethyl-branched paraffins and an isomerization zone recycle stream comprising mono-methyl-branched paraffins.

9. The process of any one of claims 1-8 wherein said first isomerization zone feed stream of step (e) is passed to a first isomerization zone containing an isomerization catalyst to selectively isomerize normal paraffins to mono-methyl-branched paraffins and dimethyl-branched paraffins.

10. The process of any one of claims 1-8 wherein said second isomerization zone feed stream of step (e) is passed to a second isomerization zone containing an isomerization catalyst to selectively isomerize mono-methyl-branched paraffins to dimethyl-branched paraffins.

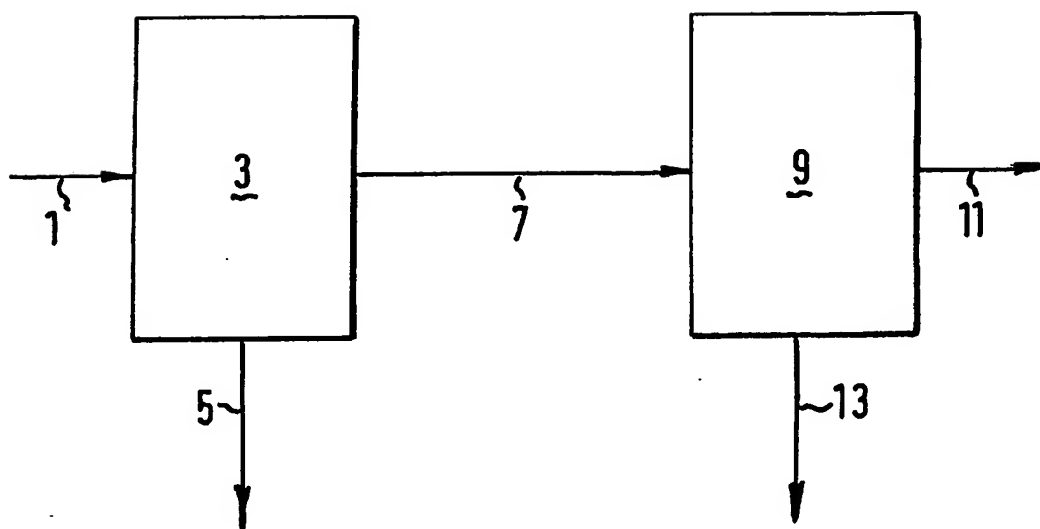
11. The process of any one of claims 1-10 wherein at least a portion of said isomerization zone effluent stream is recycled to said first and second feed separation zones.

12. The process of any one of claims 1-10 wherein said isomerization zone effluent stream is separated to yield an isomerization zone recycle stream comprising normal paraffins which are recycled to said isomerization zone.

13. The process of claim 9 or 10 wherein at least a portion of said first isomerization zone effluent stream and/or said second isomerization zone effluent stream is recycled to said first feed separation zone.

14. A process of any one of claims 1-13 wherein the first hydrocarbon feed stream comprises normal hexane, mono-methyl pentanes and dimethyl butane.

FIG. 1



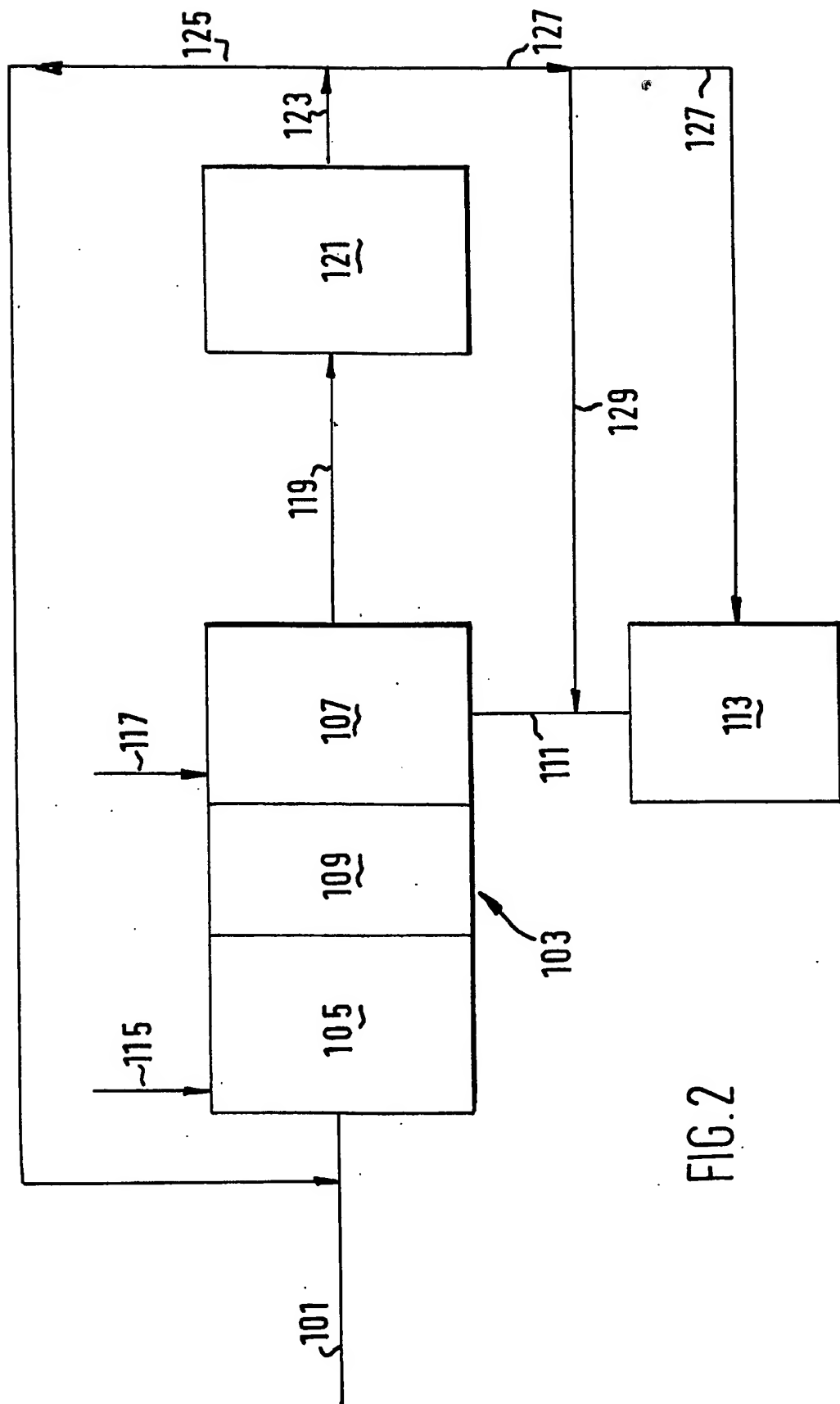


FIG. 2

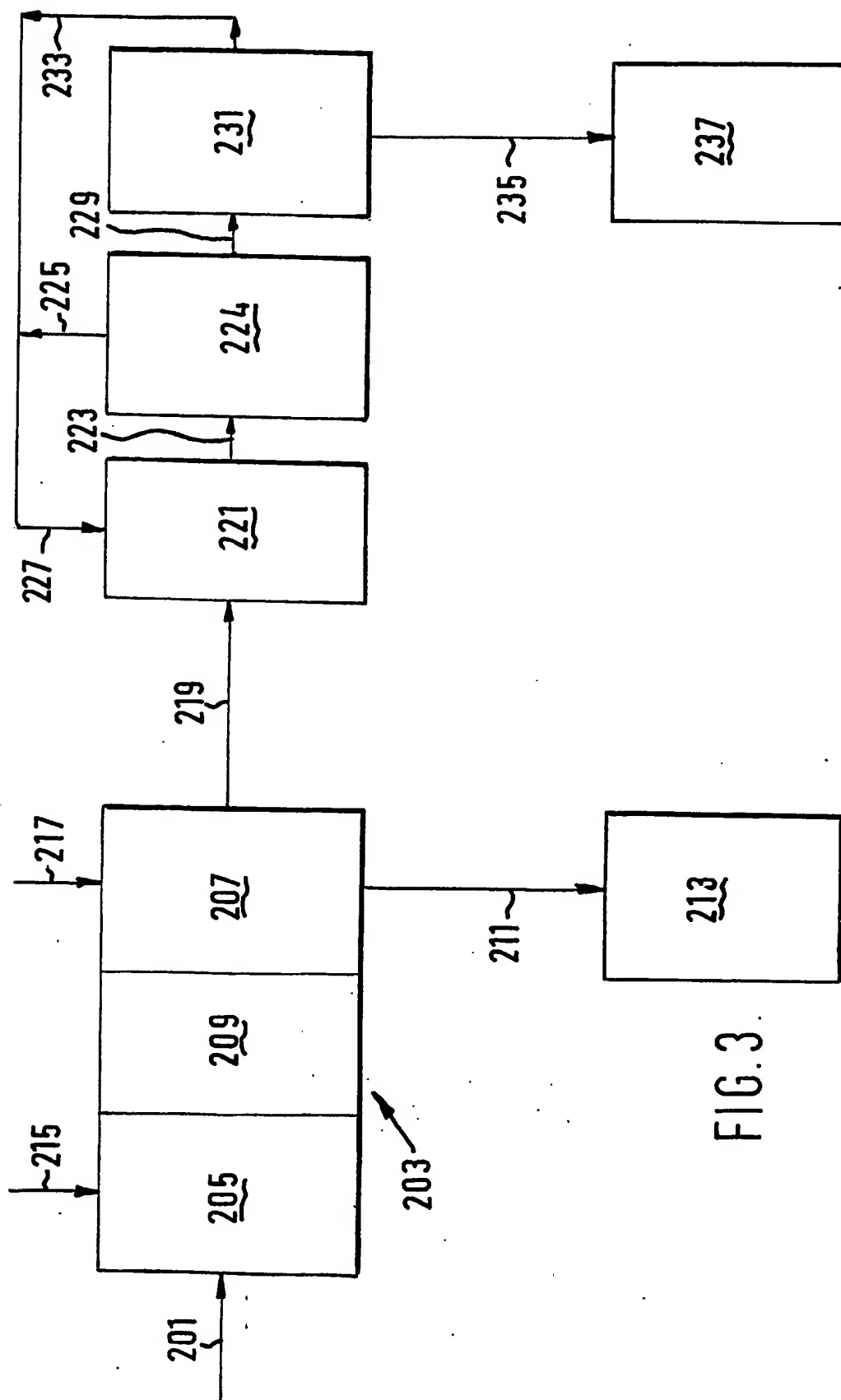


FIG. 3

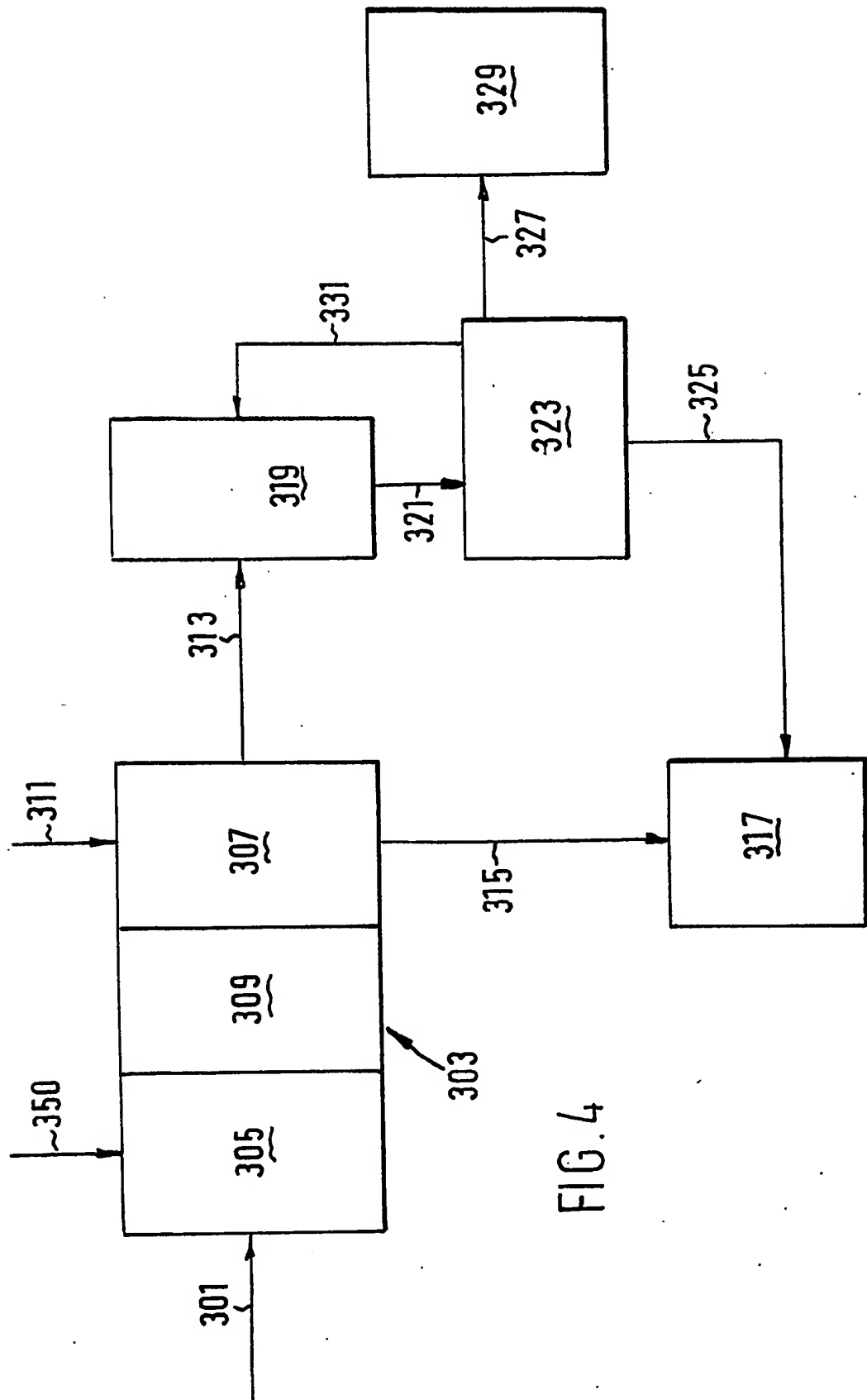


FIG. 4

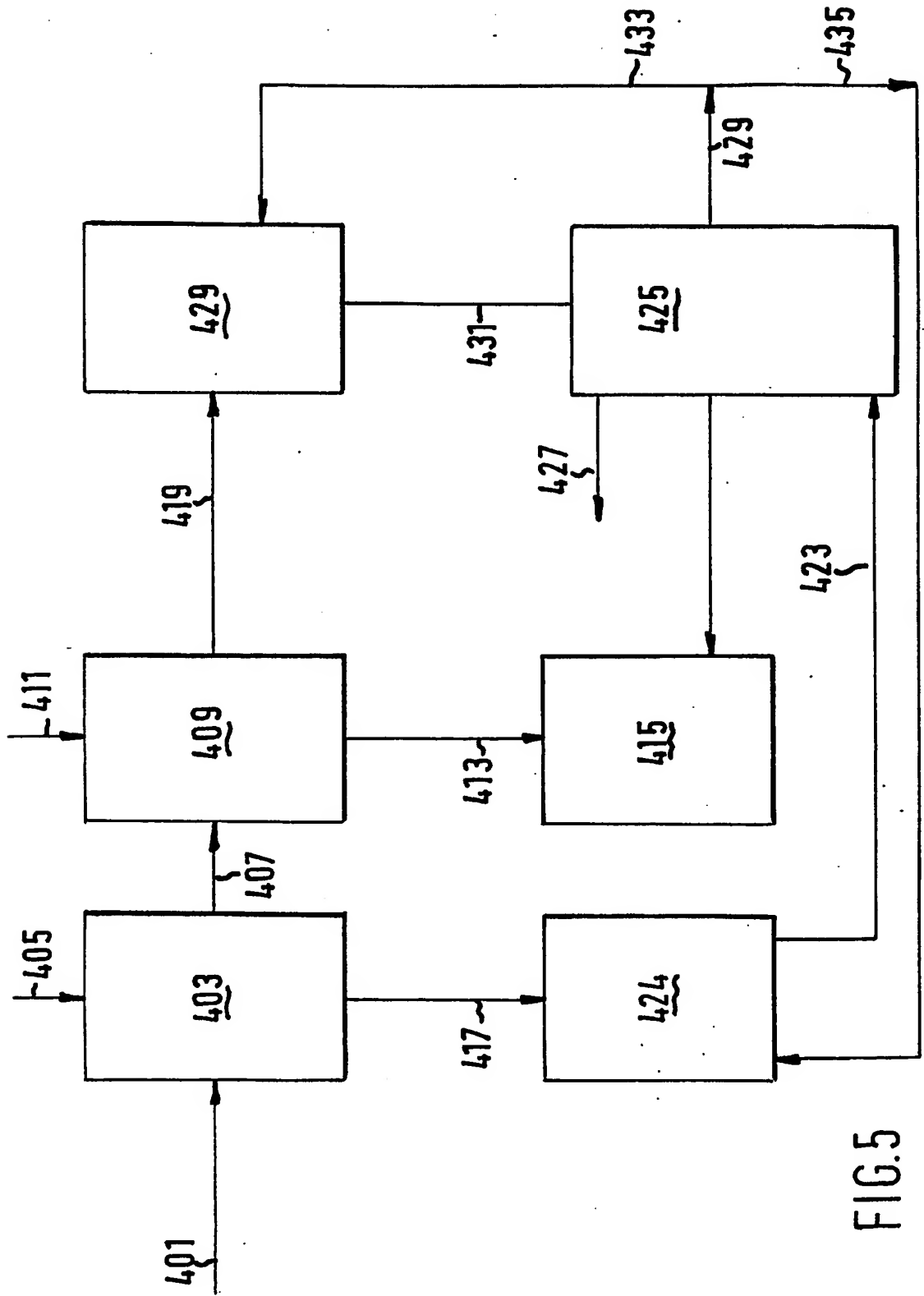


FIG.5

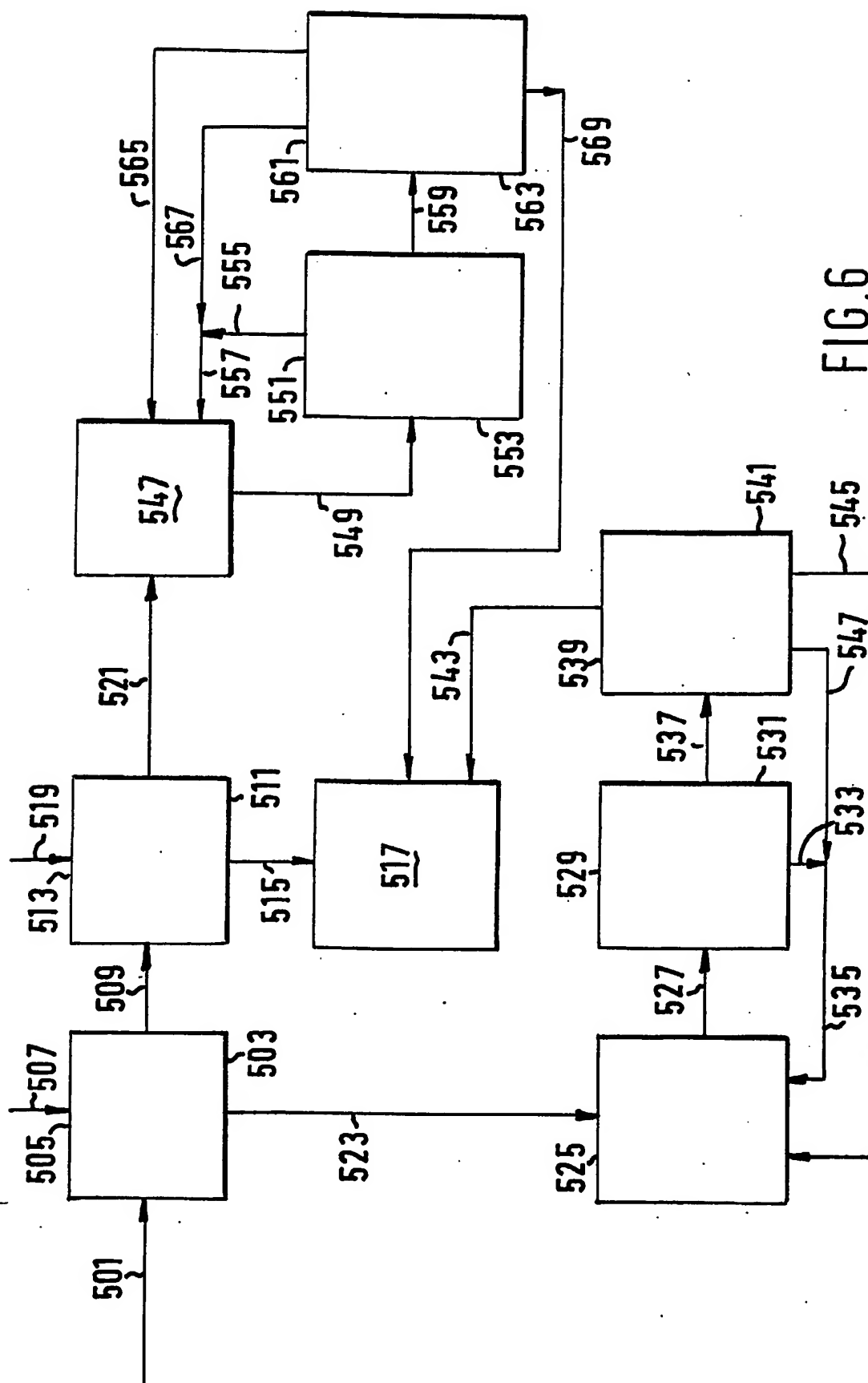


FIG. 6

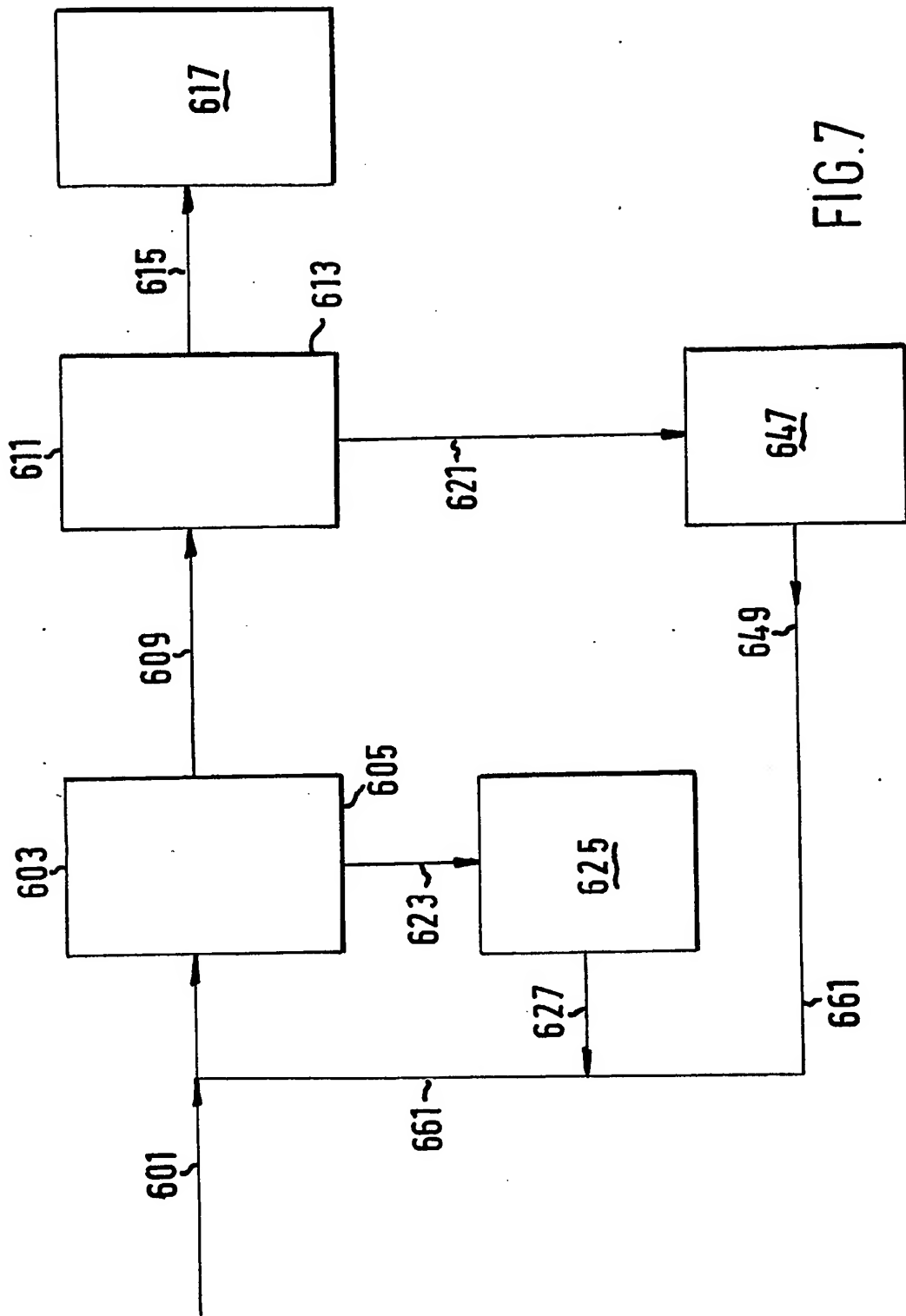


FIG. 7



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 20 0414

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 717 784 (STEM et al.) ---		C 10 G 67/06
D,A	US-A-4 210 771 (HOLCOMBE) ---		C 10 G 53/08
A	US-A-3 785 122 (YATSURUGI et al.) -----		C 07 C 7/13
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G C 07 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29-05-1990	Examiner MICHIELS P.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			